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PHYSICAL-CHEMICAL PROPERTIES OF CERAMIC MIX USING NIZHNEUVEL'SKOE CLAY

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The results of replacing Ukrainian clayey raw material with Nizhnevel'skoe clay (Russia) in ceramic mix are presented. The physical-chemical properties of the mix developed are determined. Ceramic articles were obtained with sintering temperature 1070°C with water absorption no more than 3% and total lineal shrinkage less than 13%.

Key words: physical-chemical properties of clays, ceramic mix, montmorillonite, slip casting.

Most ceramic producers in Russia use high-quality clays, which are expensive, from deposits in Ukraine. Thus the question of replacing such clays with clays from deposits in Russia in the mixes used for manufacturing ceramic articles is important.

Technological studies of the possibility of replacing in ceramic mix the “Vesko-Prima” clay from the Veselovskoe deposit in Ukraine by Nizhnevel'skoe clay from Chelyabinsk Oblast' have been performed. The “Keramika” JSC (in Glazov) uses for the production of ceramic articles with a relatively complicated shape a mix consisting of “Vesko-Prima” clay (27.2%³), Sholokovskoe clay from a deposit in Udmurtia (47.4%), nepheline-syenite (13.2%), quartz sand (8.4%), and cullet (3.8%).

Ceramic articles are obtained by slip casting in a gypsum mold. The main quality criteria for articles are water absorption, which must be no more than 3%, and total shrinkage after the second sintering (no more than 13%). The chemical composition of the clays is given in Table 1.

According to the Al₂O₃ content, “Vesko-Prima” clay is a basic clayey raw materials, while the and Sholokovskoe clays, respectively, are semi-acidic and acidic clayey raw materials. With respect to the amount of Fe₂O₃ and TiO₂ the “Vesko-Prima” and Nizhnevel'skoe clays have average and the Sholokovskoe clay high content of coloring oxides.

The behavior of clays in the “clay – water” system and during sintering is determined mainly by the sizes of the particles in clayey material, which comprise the main ceramic mix. The dispersion composition of the clays is presented in Table 2.

The dispersity also affects plasticity, binding capacity, and shrinkage of clay during drying and calcination.

The higher the plasticity of clay, the higher its binding capacity is. “Vesko-Prima” and Nizhnevel'skoe clays with plasticity number 18.2 and 16.0, respectively, have medium plasticity while the plasticity of Sholokovskoe clay (plasticity number 12) is moderate.

The nonuniformity of the shrinkage often leads to the formation of cracks. The lower the shrinkage, the lower the proneness of the clays to form cracks during drying is. This rule is expressed by the coefficient of sensitivity of clay to drying K_s . The greater K_s , the more sensitive the clay is to

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³ Here and below — content by weight.

TABLE 1. Chemical Composition of Raw Material

Clay	Content by weight, %								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	others
“Vesko-Prima”	56.90	28.50	0.9	0.55	0.46	0.46	1.93	1.38	9.00
Nizhnevel'skoe	64.20	22.20	3.00	0.63	0.30	0.30	0.59	1.20	7.60
Sholokovskoe	66.25	12.13	4.63	1.60	1.78	2.00	1.8	2.07	7.18

TABLE 2. Dispersion Composition of the Raw Material

Size fraction, mm	Fraction content, %		
	“Vesko-Prima” clay	Nizhneuvél’skoe clay	Sholokovskoe clay
More than 0.06	0.03	4.42	16.40
From 0.06 to 0.01	0.40	25.54	38.56
From 0.01 to 0.005	4.40	6.92	6.16
From 0.005 to 0.001	20.30	15.92	13.00
Less than 0.001	74.87	47.20	25.88

TABLE 3. Data from an Analysis of the Sinterability of Clays

Clay	Calcina- tion tem- perature, °C	Fire shrink- age, %	Total shrink- age, %	Water absorp- tion, %	Open porosity, %	Apparent density, g/cm ³
“Vesko-Prima”	900	0.56	6.0	15.8	26.8	1.70
	950	1.48	6.9	12.2	22.5	1.84
	1000	3.78	9.7	8.7	17.1	1.96
	1050	5.70	11.3	2.4	5.1	2.10
	1100	7.77	12.8	0.8	1.9	2.30
Nizhneuvél’skoe	900	0.67	6.9	15.3	27.7	1.82
	950	0.78	7.2	14.6	27.0	1.85
	1000	0.85	7.1	14.6	27.0	1.85
	1050	1.92	8.0	12.9	24.4	1.89
	1100	3.07	9.4	10.9	21.6	1.98
Sholokovskoe	900	0.22	8.4	11.7	22.9	1.97
	950	0.26	8.4	11.3	22.6	1.99
	1000	0.65	8.2	10.9	22.0	2.02
	1050	1.16	8.0	9.4	19.2	2.04
	1100	3.50	10.1	5.9	13.1	2.23

drying. The quantity K_s for “Vesko-Prima”, Nizhneuvél’skoe, and Sholokovskoe clays is, respectively, 0.78, 0.82, and 1.27, i.e., the “Vesko-Prima” and Nizhneuvél’skoe clays are low-sensitivity clays and Sholokovskoe clay is a medium-sensitivity clay.

The sinterability of these clays as analyzed. The Nizhneuvél’skoe and Sholokovskoe clays are nonsintering, since during calcination to 1100°C the water absorption of a sample is > 5% while the “Vesko-Prima” clay is strongly sintering — after calcination at 1100°C the water absorption of the sample is no more than 2% (Table 3).

The investigations of the replacement of “Vesko-Prima” clay by Nizhneuvél’skoe clay were conducted with three mix compositions with Nizhneuvél’skoe – “Vesko-Prima” ratios 50 : 50 (composition No. 1), 60 : 40 (composition No. 2), and 70 : 30 (composition No. 3). The preliminary experiments with “Vesko-Prima” clay completely replaced with Nizhneuvél’skoe clay showed that the water absorption of the articles after calcination at 1050°C was about 12%.

TABLE 4. Properties of Samples after the First Calcination

Mix com- position	Calcination temperature, °C	Water absorption, %	Open porosity, %	Apparent density, g/cm ³	Sample thickness, mm
No. 1	900	18.9	33.8	1.79	3.0
	1050	7.9	16.9	2.15	3.1
	1060	4.3	9.7	2.27	2.9
	1070	2.9	6.9	2.34	2.9
	1080	1.0	2.2	2.41	2.8
No. 2	900	19.7	34.8	1.77	3.5
	1050	8.3	17.8	2.15	3.4
	1060	4.9	10.9	2.25	2.5
	1070	3.1	7.4	2.34	3.6
	1080	1.5	3.6	2.39	2.8
No. 3	900	20.0	35.3	1.77	3.5
	1050	8.7	18.7	2.14	3.5
	1060	5.4	12.0	2.23	2.9
	1070	3.2	7.5	2.32	2.8
	1080	3.0	7.0	2.33	3.6

Slip based on these clays was obtained by means of the technology adopted at “Keramika” JSC. As the amount of Nizhneuvél’skoe clay in the mix increased, the thickening factor of the slip was 2, as a result of the fact that Nizhneuvél’skoe and Sholokovskoe clays contain montmorillonite, which liquefies poorly under electrolytes. For better liquefaction of the slip, aside from 0.15% of liquid glass and 0.35% soda, sodium polyacrylate (SPA) was introduced in amounts 0.42 – 0.77% into the slip [1]. The properties of the slip obtained were as follows: moisture content 41 – 45%, density 1.52 – 1.57 g/cm³, and thickening ratio 1.1 – 2.4. No defects were observed on articles when SPA was introduced.

It was established that when the content of the Nizhneuvél’skoe clay in the mix is increased, the water absorption after the second calcination at 1050°C increases and is greater than 3%. To decrease the water absorption to less than 3%, the content of nepheline-syenite in the mix was increased from 13 to 18.7%.

Samples made from slips obtained in this manner were poured into gypsum molds [2], the thickness of the sample walls being no more than 4 mm. The time required to accumulate ceramic paste in the gypsum mold was 40 – 50 min. After drying, the samples were calcined at 900, 1050, 1060, 1070, and 1080°C. Some properties of the calcined articles are presented in Table 4.

It follows from the data in Table 4 that as the content of Nizhneuvél’skoe clay in the mix increases from 50 to 70%, the water absorption of samples calcined at 900 and 1080°C increases from 18.9 and 20% and from 1 to 3%, respectively. This is because the sinterability of Nizhneuvél’skoe clay in the indicated interval is poor. However, it should be noted that the composition No. 1 after calcination at 1100°C is characterized by the following indicators: water absorption

TABLE 5. Properties of Samples Coated with Glaze after the Second Calcination

Mix composition	Calcination temperature, °C	Water absorption, %	Open porosity, %	Apparent density, g/cm ³	Sample thickness, mm
No. 1	1050	3.5	8.1	2.29	3.6
	1070	0.3	0.7	2.33	3.0
	1080	0.04	0.1	2.46	3.5
No. 2	1050	5.1	11.1	2.18	4.0
	1070	1.1	2.6	2.36	3.5
	1080	0.2	0.5	2.46	3.2
No. 3	1050	5.4	11.7	2.17	3.9
	1070	1.2	2.8	2.33	3.0
	1080	0.2	0.5	2.46	3.1

of the samples 0.06%, open porosity 0.14%, and apparent density 2.5 g/cm³.

Thus, the water absorption in samples made from composition No. 1 at calcination temperature 1080°C is 1%, which makes it possible to obtain dense articles.

The samples made from compositions Nos. 1 – 3 and calcined at 900°C were coated, by means of dipping, with a glaze on the inner and outer sides and then calcined in the interval 1050 – 1080°C. The properties of the samples are presented in Table 5.

Glazing of sample surfaces after the first calcination decreases the water absorption of samples calcined at 1050 and 1080°C from 3.5 to 0.04% and from 5.4 to 0.2% for compositions No. 1 and No. 3, respectively. For this reason, the calcination of glazed articles for the indicated compositions must be performed at 1070°C and higher. Then the water absorption of ceramic will be less than 3%.

Samples with the dimensions 50 × 50 × 10 mm were formed from mixes Nos. 1 – 3 by plastic pressing to determine the post-drying and -calcination shrinkage. The shrinkage properties were determined by the method of [3]. The results are presented in Table 6.

As the content of Nizhnevel'skoe clay in the mix increases, the total shrinkage decreases from 15.4 to 14% after

TABLE 6. Shrinkage Properties of Ceramic Mix

Mix composition	Air shrinkage, %	Calcination temperature, °C	Fire shrinkage, %	Total shrinkage, %
No. 1	5.9	900	1.1	7.6
		1060	8.9	14.7
		1070	9.0	14.4
		1080	9.4	15.4
No. 2	6.5	900	1.1	7.6
		1060	8.2	13.5
		1070	9.0	13.9
		1080	9.1	14.0
No. 3	6.7	900	0.7	7.3
		1060	8.0	13.0
		1070	9.0	13.9
		1080	9.1	14.0

calcination at 1080°C for compositions No. 1 and No. 3, respectively. In general, the shrinkage for all mix compositions decreases negligibly and remains in the range 13 – 14% as calcination temperature increases from 1060 to 1080°C.

In summary, the water absorption of ceramic articles does not greater than 3% and the total shrinkage 13% are attained by introducing into the mix 50 – 70% Nizhnevel'skoe clay (Russian) instead of “Vesko-Prima” clay (Ukraine) as well as nepheline-syenite to 18.7%. The temperature of the second (poured) calcination should not be less than 1070°C.

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